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EXPERIENCE IN THE USE OF A HYDROCHEMICAL METHOD IN POLYMETALLIC ORE PROSPECTING

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Set forth in this article are the results of checking the use of field hydrochemical methods of investigation in prospecting for ore deposits, developed by a group of specialists of the VSEGINGEO institute [All-Union Research Geological Institute of Geochemistry].

The explorations were made in a complex with other kinds of prospecting work by one of the geological parties. The area of the work occupied part of a ridge of northwest direction, maximal marks of which reach 2,500 m. In the geological structure of the perspective part of the district, tuffaceous rocks of the Eocene series play the major role, having the following section (from below up):

(1) bottom tuffoeffusive series, represented primarily by augite porphyrites which at places change to tuffs; its thickness 300 m;

(2) tuffo-residual perspective series, formed in its lower part by tuffs, which upwards along the section change to fine-stratified tuffosandstones; its thickness 300 m;

(3) level of augite porphyrites of andesite composition 150 m in thickness;

(4) second tuff level, represented by tuffosandstones and tuffs of dacite composition; its thickness 150 m;

(5) top tuffoeffusive series, represented chiefly by andesite porphyrites; thickness of this series 400 m.

From the intrusive rocks in the district of the deposit, post-ore dikes of diabasic porphyrite have been spread. The rocks are crushed in the sloping of the folds of northwest strike. The dipping of the sides of the folds usually does not exceed 30°.

Large-scale tectonic disturbance of the northwest strike is recorded among the disruptive disturbances in the district.

The polymetallic mineralization (galenite and sphalerite) which has an obviously bedded character, is timed to the layer of limy tuffosandstones of the tufforesidual series. The polymetallic mineralization changes upwards to bedded copper-hematite, and still higher, to copper-hematite disseminated.

Characteristic for the second tuff level is the presence of lode copper-hematite mineralization. Near the bedded mineralization the holding rocks are limonitized. The content in them of epidote, quartz, and carbonates is characteristic for the holding rocks.

By preceding work, it was established that the bedded ore developments are marked by brokenness and uneven distribution within the perspective series. The tasks of hydrochemical investigations in the district were the further tracing of the ore strata previously determined and the prospecting for new ones within the limits of the same perspective series.

In a hydrogeological sense all the rocks which form the district have in some degree abundant water. The tuffosandstones of the perspective series and the second tuff level have the greatest amount of watering. The porphyrites underlying these rocks are for the tuffosandstones practically a water catch; therefore the maximal number of water manifestations are adapted to their contact. According to conditions of circulation, the underground waters in the district are classed:

(1) waters of deep circulation which have plateau-form supply sources in the southeastern part of the district, where absolute marks reach up to 2,500 m;

(2) waters of shallow circulation distributed primarily in the western and northwestern foothill parts of the district. Predominant in the relief of these sections are separate small ridges and odd summits up to 2,000 m in elevation, which form local areas of supply isolated from each other; here there are no significantly sustained aquiferous levels.

The district as a whole is characterised by a substantial activity of water exchange. Here, the annual amount of precipitation reaches 700 mm, and the amplitude of the variations of absolute marks reaches 1,000 m. Consequently, a large number of springs are present.

Investigation of the chemical composition of the underground waters was done chiefly at the springs. The chemical analyses of the water were made in the laboratory of the detail on the day after sampling. The ore elements (Cu, Pb) were determined by the colorimetric method in the field laboratory.

The field investigations were conducted in several stages. In the first stage the general chemical composition of the district's underground waters was investigated with the object of ascertaining the conformities to principles in formation of the chemical composition of the district's underground waters, and also the connection of the lithological composition of the rocks with the general chemical composition of the underground waters that occur under the influence of mineralisation.

In consequence of the analysis, it was established that in the district of the investigations the underground waters outside the mineralised rocks possess slight mineralisation, chiefly up to 200 mg/l with the following average content of the main ingredients of mineralisation:

Cl	3.8 mg/l
SO_4	6.0 mg/l
HCO_3	100 mg/l
Ca	100 mg/l
Mg	10 mg/l
Na	10 mg/l
pH	6.7-7.3

The content of the indicated ingredients of mineralisation in the underground waters, adapted to various stratigraphic complexes, does not undergo significant variation, with the exception of an increase in the content of SO_4 ion in the waters of the second tuff level, which will be discussed later.

The maximal contents of lead in waters outside of known sections of ore deposits reaches 0.01 mg/l, of copper 0.02 mg/l. The low contents of ore elements in the water are apparently to be explained by the heightened activity of water exchange, which brings about intensive dissipation of the ore elements in the underground waters, in contrast to lowered activity of water exchange, under which conditions the accumulation of ore elements occurs to a certain limit in underground waters.

The content of lead in the district's underground waters proved close to the sensitivity of the colorimetric method. Therefore, the distribution of lead in the underground waters of separate sections had to be compared not by quantitative ratios but only by percentages of occurrence.

We will dwell on the contents in the water of Cu and Pb according to various stratigraphic complexes. This comparison was made by percentages of occurrence and points for copper and by percentages of occurrence for lead. The content of copper in points was evaluated as follows:

Content of Cu in mg/l	Points
Traces	0.5
0.01	1.0
0.02	2.0

The distribution of ore elements in waters that had no connection with mineralized rocks was subject to the following hydrochemical principle. The waters of the lower tufforesidual series have the greatest percentage of lead occurrence, the waters of the second tuff level possess heightened contents of copper, the percentage of occurrence and points of which rise regularly to the top of this level.

We cite the data of the contents of copper and lead in the underground waters, distributed outside mineralised rocks in the various stratigraphic levels (Table 1).

Inasmuch as heightened activity of water exchange, under the conditions of which only leaching occurs, is characteristic of the district, then such an uneven distribution of ore elements in the underground waters of the indicated complexes is to be explained by the varied intensity in the rocks of dispersed mineralization of ore elements in sulfide form.

TABLE 1

Name of Complex	Percentage of occurrence Cu	Points of Cu	Percentage of occurrence Pb
Tufforesidual perspective series	68.4	0.5	16
Second tufforesidual level:			
sublevel 1	33.0	0.25	0
sublevel 2	83.0	0.40	0
sublevel 3	100.0	1.25	12.5
Top tuffoeffusive series	22.0	0.10	5

With respect to the content of sulfites in the underground waters of the various lithological complexes, it should be noted that the waters of the second tuff level possess the greatest magnitudes of the sulfate ion (on the average 8 mg/1), in contrast to the waters of the tufforesidual perspective series, where the content of sulfate ion is but 4.2 mg/1. This is evidently the intensity, relatively heightened for the given district, of dispersed copper mineralization, peculiar to the second tuff level.

The second stage of the hydrochemical field investigations consisted in the study of variations of the chemical composition of the underground waters under the influence of certain rocks known to be mineralized. It should be stressed that the district described has favorable conditions for the study of the influence of mineralization on the chemism of waters, inasmuch as the maximal number of natural water manifestations are adapted to the contact of tuffosandstones (potentially ore-bearing) with the underlying porphyrites which are a water catch.

The effect of mineralization on the chemical composition of underground waters is expressed chiefly in the increase of their sulfate content. Increase in the contents of ore elements in underground waters near mineralisation is not observed. This is a consequence of the previously examined uneven distribution of dispersed sulfide mineralization (outside mineralised rocks) in various complexes of rocks in combination with the heightened activity of water exchange which brings about intense dispersion of ore elements in the district's area. It was established by investigations that the percentages of occurrence of ore elements in waters close to mineralized rocks and outside them are approximately identical. Thus, the content of ore elements in the underground waters in the district being described cannot serve as a direct indication of the presence of ore deposits in one or another section. However, the prospects of the given lithological complex can be determined for the given district according to the content of ore elements in the underground waters, since the lower tuff level can be practically distinguished from the upper according to the percentage of occurrence of ore elements (Cu and Pb), i.e., distinguishing the strata which are potentially polymetal-bearing from the oreless second tuff level, the more so since they are hardly distinguishable from each other visually. This problem was practically solved according to the percentages of copper occurrence in the waters. During detailed geological investigations the sections with considerable percentages and points of Cu usually proved to be formed with rocks of the upper tufforesidual level. As results of the work showed, the most precise ore developments in the district are fixed by the sulfate content of the underground waters. Relatively to the general growth of mineralisation, scales of the increase of sulfate content were fixed by means of the ratio of contents $\frac{SO_4}{Cl}$ in mg/l. It is possible to apply this coefficient for the initial stage of the formation of the chemical composition and in a small interval of it, when the magnitudes SO_4 and Cl increase approximately to the same extent. For districts with waters in various stages of the formation of chemical composition, which have substantial amplitudes of variation of general mineralization, this factor for evaluating prospects is not applicable. In order to ascertain how the sulfate content of the waters is changed in time, a network regime of 3 springs was set up in the district. It was learned that in proportion to decline in yield of the springs the general mineralization of the waters in them is increased, the increase in the magnitude of SO_4 rising more intensively than the increase in the content of Cl. Thus, during the 2 months (July and August), the content of SO_4 in one of the springs outside the sections of mineralization increased from 3 to 8 mg/l with the magnitude of Cl a constant 3.5 mg/l.

In this connection, during the same length of time the value of the factor $\frac{SO_4}{Cl}$ also changed from 0.8 to 2.1. If, for example, in July when the factor was equal to 2.0, this pointed to a rise of sulfate content on account of external causes, then in September such sulfate content was the consequence of the natural formation of the chemical composition of the underground waters. In the district described the magnitude of the factor for underground waters not connected with ore formations varied from 1.00 for underground waters of the bottom perspective tufforesidual series to 1.6 for waters of the top tuff level (the value of the factors are given for the second 10 days of July). Under the influence of ore formations the magnitude of the factor $\frac{SO_4}{Cl}$ was more than 2 in July. During the summer period the minimal value of this prospecting factor was increased from 2 to 3, and for the conduct of prospecting it was necessary to know the normal magnitude of the factor $\frac{SO_4}{Cl}$, which is thus a sliding scale. By regime observations it was established that the variation of sulfate content in time occurs only for waters of shallow circulation (waters of the second type).

The sulfate content of waters of deep circulation remained without change during the course of the entire summer. Thus, in using the factor $\frac{SO_4}{Cl}$ for conducting prospecting, it was essential to know the variations of its magnitudes depending on general geological and hydrogeological conditions and times.

Concerning the pH of underground waters, it should be pointed out that this magnitude for the given conditions did not undergo any kind of changes under the influence of mineralization, which again is connected with the heightened activity of water exchange.

Thus, in consequence of the second stage of investigations it was ascertained that the main hydrochemical sign which points to the presence of ore formations in the described district is the heightened ratio in underground waters of $\frac{SO_4}{Cl}$, which is traced from known ore formations in the stream of underground waters at distances up to 30. m. A favorable feature in this respect is the absence in the district of other processes which bring about increased sulfate content of the underground waters.

A secondary (auxiliary) hydrochemical sign is the content in the underground waters of ore elements, the percentage of occurrence of which points for each section to the qualitative composition of the mineralization.

In the process of field work it was ascertained that under the influence of mineralization the chemical composition not only of underground waters, but also of surface waters is changed, since the underground waters play the predominant role in the supply of small brooks. The sampling of brooks, in the valleys of which mineralisation is known, showed the regular increase of the sulfate content of surface waters (Figures 1, 2). The chemical composition of surface waters could in individual cases also be used in the capacity of an auxiliary hydrochemical prospecting sign.

The third stage of the hydrochemical investigations consisted in the promotion of prospecting proper which was done according to the data of the second stage investigations. However, it should be noted that prospectings can be conducted, omitting the second stage of investigations, immediately after ascertaining the general principles of the formation of the chemical composition of the waters of the district. Field investigations are thereby considerably complicated.

Prospectings by the hydrochemical method must be done without fail in a complex with geological operations supplementing them. The hydrochemical method must not be regarded as something independent; this is a secondary method, but it can greatly facilitate the work of prospecting fo ores.

The shortcoming of the method is only that it can be applied solely in districts with a dense system of natural water developments. The density of points is an essential condition for the hydrochemical method. The number of points can be increased by means of light mining operations (diggings, etc).

The prospecting method of the third stage of investigations consisted of the following. At sections of the development of perspective tufforesidual series, simultaneously with the staging by geologists of the alluvial sand method, mass sampling of underground and surface waters was carried out. Proceeding from the magnitude of the hal- of dispersion of sulfates in the underground

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waters, specimens were taken wherever possible not less frequently than every 300 m. Otherwise, it would have been impossible to draw any kind of definite conclusions on the section sampled. The surface waters were tested from the mouth to the source. Both complete and incomplete analyses were made. In general complete analyses are essential only at the initial stages of operations (the stages 1 and 2), when investigations are being made to find hydrochemical signs. In the conduct of prospecting it is more desirable to make analyses only for ingredients that can point to ore formations. In the third stage of operations we did incomplete analyses which embraced the determination of pH, Cl, SO_4, Cu, Pb, Fe ··, Fe···, the determination of SO_4 and Cl being done directly enroute by means of a field laboratory.

In consequence of the hydrochemical field investigations, a map was drawn up of the prospects of the district's area. Part of this map is depicted in Figure 3. Indicated on the map are sections of hydrochemical anomalies according to the values of the factor $\frac{SO_4}{Cl}$, the average value of 2.5 being taken for the minimum value of the factor of anomaly.

The majority of anomalous sections found in the process of hydrochemical investigations were confirmed by the works of geologists. For example, an anomaly in one of the northwestern sections of the development of the perspective series, which was expressed in the increase of the value of the prospecting factor $\frac{SO_4}{Cl}$ to 2.6 in combination with an increased percentage of the occurrence of lead in the waters, was confirmed by the prospecting operations. Subsequently the polymetallic ore formation was bared by drill pits and tunnels. In the eastern part of the perspective district a large group of anomalous values of the factor $\frac{SO_4}{Cl}$ (up to 5 or 6), were confirmed by the detailed works of geologists, who established in this part of the district a number of bedded polymetallic ore formations.

In conclusion it is necessary to note that the hydrochemical prospecting criterion cited above, as well as the method of conducting the operations, can be used above all in districts that have natural conditions similar to those described.

It is essential to consider that in every definite district the hydrochemical prospecting signs can possess a certain specific character. These singularities must be established on the basis of an investigation of the principles of the chemism of the district's underground waters. Substantial contents in the underground waters of ore elements and of sulfates in combination with low value of the waters' pH magnitude are frequently taken in the capacity of hydrochemical prospecting criteria. Such prospecting signs are characteristic chiefly for the mine waters of copper-pyrite deposits (1, 6). In natural conditions they are rarely encountered and are usually characteristic for copper-pyrite deposits.

But prospecting for polymetals can be done with ordinary waters and even with waters of very slight mineralization, as happened in the district explored.

Thus, at a concrete object we succeeded in checking the possibility of employing the method of hydrochemical prospecting which is being elaborated by a group of specialists of the VSEGINGEO Institute. It is necessary to check this method in other districts also, so that complex prospecting for ore deposits be then more widely installed in practice.

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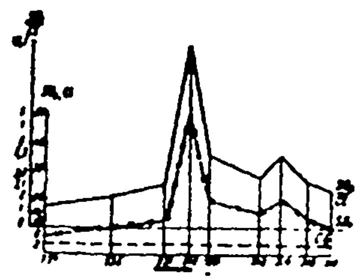
FIGURES



Hypotehtical mineralization in side of valley

Figure 1. Variations of the magnitudes of factor $\frac{SO_4}{Cl}$ and content of CO_4 and Cl along course of brook I-I

Mineralization in sides of valley

Figure 2. Variation of the magnitudes of factor $\frac{SO_4}{Cl}$ and content of CO_4 and Cl along course of one of the district's brooks

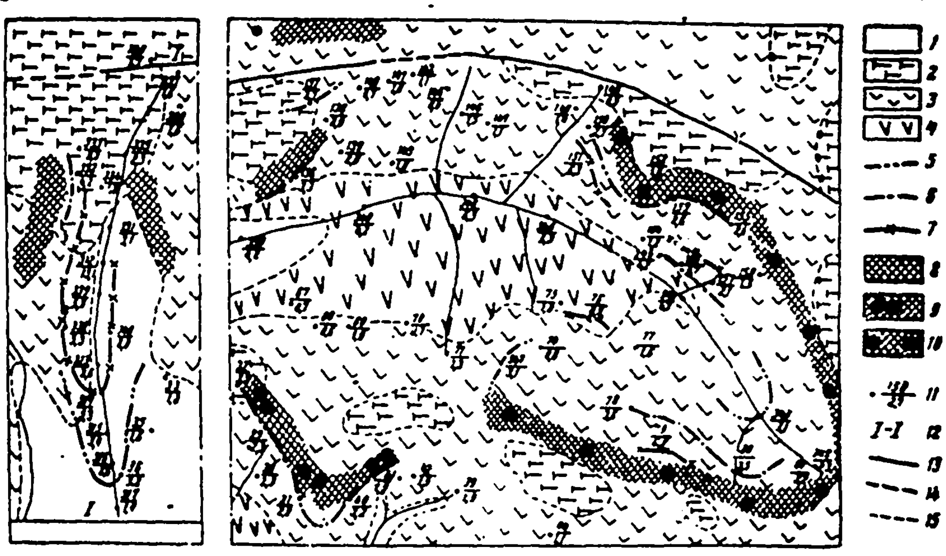


Figure 3. Diagram of prospects of one of districts prospected. 1. alluvial-deluvial measures Q; 2. porphyrite level; 3. level of ore-bearing tuffosandstones; 4. bottom tuffoeffusive level; 5. value of the factor $\frac{SO_4}{Cl}$ 2.5-3.5; 6. value of the factor $\frac{SO_4}{Cl}$ 3.6-4.5; 7. value of the factor $\frac{SO_4}{Cl}$ 4.5; 8. hypothetical sections of mineralization according to the results of the hydrochemical investigations; 9. mineralization known before the start of field operations; 11. numerator, number of tests; denominator, value of factor $\frac{SO_4}{Cl}$; 12. contour of variation of sulfate content of surface waters; 13. visible tectonic disturbances; 14. presumed tectonic disturbances; 15. contacts